

EFFECT OF CHLOROBENZENE PRE-TREATMENT ON MACROMOLECULAR STRUCTURE OF BITUMINOUS COALS

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ABSTRACT

Recent work has demonstrated that chlorobenzene (CB) pre-treatment can affect the mass transfer characteristics of Pittsburgh No.8 Argonne Premium Coal Sample (APCS), as indirectly it results in significantly altered product yields in a number of liquefaction regimes. Pre-treatment of Pittsburgh No.8 APCS with CB results in significant conformational changes and this is then reflected by examination with differential scanning calorimetry (DSC), surface area (SA) measurement and broadband ^1H NMR relaxation. DSC reveals the existence of a glass to rubber transition (T_g) for untreated and treated samples in the region 110°C to 120°C, with the transition shifted to a lower temperature for the CB treated coal. CO_2 adsorption indicates that CB treatment markedly affects the amount of CO_2 adsorbed and the equilibration behaviour. The chlorobenzene treatment caused the ^1H thermal relaxation times to generally increase, in contrast to pyridine extraction where the reverse trend is usually observed.

INTRODUCTION

It has been previously summarised that in cases where improved liquid product yields had been achieved in coal liquefaction⁽¹⁻⁸⁾, the accessibility of solvents within the highly porous macromolecular structure of coals has been improved, particularly during the initial stages of liquefaction where retrogressive reactions need to be avoided. However, interpretation of these phenomena in terms of changes in the macromolecular structure of coals is complicated by the fact some organic matter is being removed at the same time that conformational changes may be occurring. Chlorobenzene has the advantage of extracting virtually no organic matter from coals. Further, it is non-polar and would not be expected to significantly disrupt hydrogen bonds at relatively low temperatures (<150°C) in coals.

It was found that the chlorobenzene treatment improved the oil yields (as measured by dichloromethane-solubles) in short contact time hydrogen-donor solvent liquefaction with tetralin (400°C, 15 min.) for the 3 bituminous coals^(9,10). As well as short contact time liquefaction with tetralin, improved oil yields were also achieved upon chlorobenzene treatment in solvent-free (dry) hydrogenation of Pittsburgh No. 8 coal⁽⁹⁾. The amounts of hydrogen transferred from the tetralin were broadly similar for the initial and chlorobenzene-treated coals strongly suggesting that the improved oil (DCM) yields arise from limiting retrogressive char-forming reactions rather than cleaving more bonds *per se*. However, the increased oil yields were accompanied by reductions in the overall conversions to pyridine-solubles for two out of the three bituminous coals investigated. Reducing the pre-treatment time from the standard 3 day period to 3 hours for Point of Ayr gave similar conversions with tetralin indicating that the conformational changes occur relatively fast, particularly in relation to the timescales of over 3 days usually associated with completely removing solvent-extractable material. This trend would appear to be consistent with the recent communication by Larsen and

co-workers⁽¹¹⁾ who found that the chlorobenzene treatment reduced the yield of pyridine-insolubles from tetralin extraction of the Illinois No. 6 APCS.

In the continuing investigation into the effects of chlorobenzene treatment on coal conversion phenomena, the effect of the pre-treatment on the macromolecular structure has been investigated using DSC, broadband ^1H NMR and CO_2 adsorption. Further liquefaction experiments have been conducted using hydrogenated anthracene oil and solvent free hydrogenation. Point of Ayr coal under relatively low temperature pyrolysis was conducted to ascertain whether the same effect occurred as pre-treating with chlorobenzene.

EXPERIMENTAL

The standard chlorobenzene treatment of 3 days was applied to the coal samples of Point of Ayr (87% dmmf C), Bentineck (83% dmmf C) both of which are UK coals and Pittsburgh No. 8 APCS. As previously described with tetralin, extractions with HAO and hydroliquefaction with naphthalene were conducted with a solvent to coal mass ratio of 2:1 and contact times of 15 and 60 min. at 400°C , yields of DCM- and pyridine-insolubles being determined. Pyrolysis of Point of Ayr was conducted in a tube furnace. The sample was heated up to 180°C at a rate of 5°C min^{-1} under nitrogen then cooled to room temperature, the volatile matter property was then compared to that of the CB treated coal.

DSC was carried out on the initial and chlorobenzene-treated samples of the Pittsburgh No. 8 APCS using a Mettler DSC 30 system. The standard aluminum pan used contained two holes which allowed the evaporation of water. Each sample was weighed into the aluminum pan and then dried under a stream of nitrogen at 110°C before being cooled to 30°C and reweighed. DSC was then performed by heating the sample at $10^\circ\text{C min}^{-1}$ to 250°C .

^1H NMR thermal relaxation times (T_1 s) were determined at 100 MHz using the Bruker MSL 100 spectrometer by inversion recovery using single point acquisition for the free induction decays. 128 delays were used with fixed increments of either 6 or 10 ms. The data were fitted either to a single or two components using the SIMFIT Pascal programme; the smaller increment of 6 ms gave more data points covering the initial relaxation and this favoured a two component fit.

To determine the effects of chlorobenzene treatment on rates of mass transfer, CO_2 adsorption at 19K and a P/P_0 of 0.05 was measured using a Quantasorb Quantachrome instrument.

RESULTS AND DISCUSSION

Volatile Matter

Table 1 shows the volatile matters for initial coal, chlorobenzene treated coal and the pyrolysed coal (180°C). The value has remained within experimental error indicating that the volatile matter has not been altered during either of the treatments. Therefore any change in yields for the CB treated coal can be accounted for by a change in the macromolecular structure.

Hydrogenated anthracene oil extractions

The yields obtained from the initial and chlorobenzene-treated samples of Point of Ayr and Bentinck coals with residence time of 60 min. are summarised in Table 2. The effects of the pretreatment on conversions are relatively small for Point of Ayr coal, especially compared with tetralin^(9,10). In contrast, significant reduced overall conversions to pyridine-solubles have been obtained for Bentinck coal with a concomitant reduction in oil yield at the longer residence time (Table 2).

HAO is largely in the liquid phase at 400°C and, intuitively, should be affected less by conformational changes brought about by the chlorobenzene treatment than smaller molecules in the vapour phase, such as tetralin. Nonetheless, mass transport phenomena would still appear to be affected, particularly for Bentinck where the ability of HAO to prevent retrogressive reactions has been curtailed.

Batchwise hydrogenation

Table 3 lists the conversions obtained for Bentinck coal. In contrast to Pittsburgh No.8 coal⁽⁹⁾, a reduced yield of DCM-soluble products was obtained upon treatment which would appear to be consistent with the general trend reported above in naphthalene hydroliquefaction. This presents further evidence that the effects of the chlorobenzene-treatment on the liquefaction behaviour of Bentinck are markedly different to those for Pittsburgh No.8 and Point of Ayr coals.

Naphthalene hydroliquefaction

The trends in naphthalene hydroliquefaction (70 bar cold hydrogen pressure) mirror those observed in the previous thermolytic extraction (Table 4) although the conversions to DCM-solubles are considerably higher due to the hydrogen over-pressure. For Point of Ayr coal, a small increase in the DCM-soluble product yield was obtained whereas, in contrast for Bentinck, there was a reduced overall conversion to pyridine-solubles (Table 4).

Differential Scanning Calorimetry

The traces from the first 3 cycles of the experiments in which initial and chlorobenzene-treated Pittsburgh No.8 coal were heated and cooled repeatedly are shown in Figure 1. The initial coal displays a broad feature centred at ca 145°C but, after heating to 250°C, this shifts irreversibly to much lower temperature (105-115°C) where it becomes truly reversible; the traces for the second and all subsequent heating cycles are virtually identical (Figure 1) and hence the event is characteristic of a glass to rubber transition. This behaviour was also recently reported by Mackinnon and Hall for the Illinois No.6 APCS⁽¹²⁾ and is broadly similar to that for many polymer systems which first of all undergo an initial enthalpy relaxation before displaying reversible glass to rubber transitions.

After chlorobenzene treatment, the initial irreversible transition observed for the parent coal is no longer present. The trace comprises a broad endotherm below 120°C which might be due to the evaporation of a small amount of residual solvent and a much sharper feature at 140°C. Upon subsequent heating, these features disappear and the traces obtained resemble those for the initial coal except the reversible glass to rubber transition has shifted ca 10°C lower (Figure 1).

This evidence confirms that chlorobenzene treatment has altered the conformation of the coal but, as for the initial coal, the treated coal then itself undergoes a further

irreversible change upon heating. The final conformation obtained may be somewhat different than that derived from the initial coal because of the lower reversible glass to rubber transition temperature.

Broadline ^1H NMR

Table 5 lists the ^1H T₁s for the 3 bituminous coals before and after chlorobenzene treatment. The thermal relaxation behaviour of the Pittsburgh No.8 APCS was best fitted to two components. Upon treatment, there is a significant increase in ^1H T₁s for Pittsburgh No. 8 (for the slower relaxing dominant component) and Point of Ayr coals but not for Bentinck. It is interesting to note that upon pyridine extraction, there is usually a marked reduction in ^1H T₁s probably due to a combination of removing molecular species and the formation of new non-covalent (hydrogen-bonded) cross-links. However, upon prolonged vacuum drying, it has been found that the increase again implying that only a small amount of pyridine imbibed is required to significantly reduce the segmental motions (frequencies in the MHz range) within the macromolecular structure. Thus, the implication is that the chlorobenzene treatment has increased the mobility (possibly through the irreversible cleavage of non-covalent cross-links) within the macromolecular structure of two out of the three bituminous coals investigated.

CO₂ Adsorption

Following CB treatment Pittsburgh No.8 and Point of Ayr showed an increase in the equilibrium uptake of CO₂. The relative increase for Pittsburgh No.8 was 1.77 and for Point of Ayr 1.43. These results are difficult to interpret unequivocally but it is known that CO₂ swells coals at high pressures. Therefore, the increase in CO₂ uptakes may indicate an increased propensity to swell in CO₂, which may increase accessibility. Whatever the correct explanation may be, this may have important consequences for the accessibility of other materials important to liquefaction. Kinetically, the adsorption of CO₂ could be resolved into two distinct components: an initial rapid uptake was followed by a slower but more linear approach to equilibrium. After treatment, the exponential uptake proceeded more rapidly but the linear uptake region was not affected. This description extends the earlier data reported by PJH for Upper Freeport coal ⁽¹³⁾ in showing that both the amount adsorbed and equilibration behaviour are markedly affected by chlorobenzene treatment. We have attempted to model the uptake by a number of diffusion models but with no success, this may indicate mixed modes of diffusion occurring concurrently.

General Discussion

It is now evident from the wide range of liquefaction experiments conducted on the 3 bituminous coals investigated that chlorobenzene treatment profoundly affects behaviour. Further, conversions are affected both as a function of both the liquefaction regime and the coal used. These findings imply that the conformational changes brought about by the treatment are not uniform and consequently the transport properties of reactants (i.e. solvents and hydrogen gas) in and products out of reacting coals are affected in different ways.

DSC, broadline ^1H NMR and CO₂ adsorption have all detected changes with DSC indicating that the initial and chlorobenzene-treated coals undergo irreversible but different transformations in the temperature range 130-150°C. Further, DSC has raised the issue as to how the effects of chlorobenzene and, indeed other solvent treatments, might differ than those brought about by simple heat-treatment. Other techniques that

can be used to probe these phenomena include small-angle X-ray scattering (SAXS), mechanical tests and simple swelling measurements. Yun and Suuburg have recently used dynamic mechanical analysis (DMA) to detect irreversible conformational changes brought about mild heating of the Pittsburgh No.8 and Upper Freeport APCs with the results being compared with DSC and solvent swelling^(14,15). They argue that DMA measurements are considerably more sensitive than DSC below 100°C for detecting changes induced by the removal of moisture with a transition at 60°C being observed for Pittsburgh No.8 coal. However, the events observed after heating the initial coal to 200°C do not appear to correspond to those found here by DSC for CB treatment.

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Table 1 Volatile Matter for the Point of Ayr Samples

	%daf coal % V.M
Initial coal	30.0
CB-treated coal	31.3
Pyrolysed coal	29.5

Table 2 Hydrogenated Anthracene Oil Extractions with a Contact Time of 1 Hour

	%DCM conv.*	%daf coal %Pyr-sols/DCM-insols	% Pyr-insols
Point of Ayr (a)			
Initial coal	39.6	39.9	20.5
CB treated coal	38.9	43.5	17.6
Bentinck (a)			
Initial coal	54.1	42.3	3.6
CB treated coal	40.8	41.9	17.3

Table 3 Hydrogenation of Bentinck Coal (1 Hour Residence Time)

	%DCM conv.*	%daf coal %Pyr-sols/DCM-insols	% Pyr-insols
Initial coal (a)	22.2	22.6	55.2
CB-treated coal (a)	12.9	31.9	55.2

Table 4 Hydroliquefaction using Naphthalene (1 Hour Residence Time)

Coal	%DCM conv.*	% daf coal %Pyr-sols/DCM-insols	% Pyr-insols
Point of Ayr (a)			
Initial coal	29.3	36.8	33.9
CB treated coal	35.4	28.3	36.3
Bentinck (a)			
Initial coal	27.3	31.2	41.5
CB treated coal	27.9	19.0	53.1

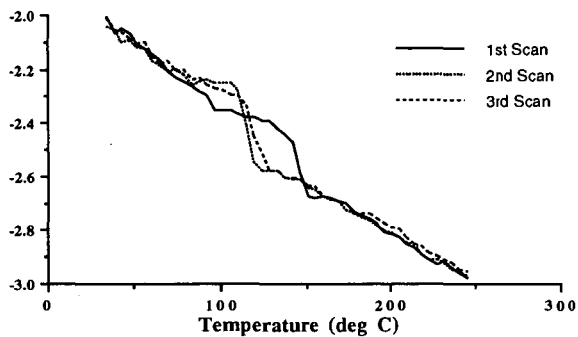
* = 100 - % DCM-insols, includes DCM soluble liquid product + gas + water.

(a) = mean of duplicate runs.

Table 5 ¹H Thermal Relaxation Times (T₁s) for Initial and Chlorobenzene-Treated Coals

Coal	T ₁ s, ms	
	Initial	CB-treated
Pittsburgh No.8	176 (82%)	198 (72%)
	7.3 (18%)	7.3 (28%)
Point of Ayr	76 (100%)	109 (100%)
Bentinck	90 (100%)	89 (100%)

Heat flow (mW) Untreated Pittsburgh No.8



Heat Flow (mW) Chlorobenzene treated Pittsburgh No.8

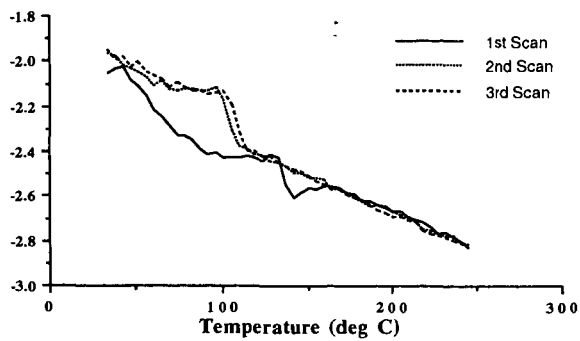


FIGURE 1 DSC ANALYSIS OF PITTSBURGH No.8 COAL